DPST-80-332

ACC. NO. 142281

DIFFUSIVITY OF HOLLOW CYLINDER

MARCH 27, 1980

BY: M. W. LEE

This document was prepared in conjunction with work accomplished under Contract No.
DE-AC09-76SR00001 with the U.S. Department of Energy.

TABLE OF CONTENTS

Introduction

Permeation measurements using hollow cylinder apparatus have frequently been analyzed by the solution of Fick's diffusion equation in planar geometry. The error of the planar approximation to hollow cylinder geometry have never been fully investigated.

In this report the solution of the diffusion equation for hollow cylinder is derived. The results are compared with planar geometry and the error range has been calculated.

Summary and Conclusion

1. The relative error in diffusivity calculated by a planar treatment of data from hollow cylinder measurements is 0.65% when the radius ratio is 0.6. The error increases as the ratio decreases.

2. This error (0.65%) is far below normal experimental uncertainty which is in the range of 3-5%.

3. Planar geometry approximation are justified for radius ratios larger than 0.6, which cover most experimental work done in the permeation study.

Discussion

The solutions of Fick's law of diffusion have been studied extensively for various boundary conditions[1-3]. Permeation tests are usually conducted by "Breakthrough" and "Pump-out" methods. In the "Breakthrough" method, both sides of a sample are evacuated initially. Applying a fixed pressure of gas on one side, the flow rate is then measured on the other side of the sample until steady state is reached. In the "Pump-out" method one side of a sample is under a fixed pressure and the other side is under vacuum. In this case the flow rate of gas through the sample is at steady state to begin with. Pumping out quickly on the high pressure side, the flow rate is then measured repeatedly on the initially evacuated side until the flow reaches a minimum value measurable.

The relative flow rate to that at steady state for hollow cylinder geometry can be formulated as

$$Y = -2 \ln \left(\frac{b}{a}\right) \sum_{n=1}^{\infty} \frac{Jo\ (a\alpha_n)\ Jo\ (b\alpha_n)}{Jo^2(a\alpha_n)-Jo\ (b\alpha_n)} \exp\left[-\ \alpha_n^{\ 2}\ Dt\right]$$

where a and b are inner and outer radius of hollow cylinder, respectively, Jo is the bessel function [4] of the first kind, D is diffusivity and α_n's are the eigen values of the equation

$$Jo\ (a\alpha_n)\ Yo\ (b\alpha_n) - Jo\ (b\alpha_n)\ Yo\ (a\alpha_n) = 0$$

The Yo is "Bessel function" of the second kind. For "Breakthrough" experiments y is defined by

$$y = \frac{Js - J\ (t)}{Js}$$

and for "Pump-Out" it is

$$y = \frac{J\ (t)}{Js}$$

Js and J (t) are the flow rates at steady state and at time t, respectively. The details of the derivation of the equations are in Appendix A.

The planar geometry solution has

$$y\ plann = 2 \sum_{n=1}^{\infty} (-1)^{n} \exp \left[\frac{n^2\pi^2 Dt}{(b-a)^2}\right]$$

where (b-a) is the thickness of the sample.

The ratios of exponents in cylindrical and planar equations.

$$\left[\alpha_n{}^2 Dt\right] \Big/ \left[\frac{n^2\ \pi^2 Dt}{(b-a)^2}\right]$$

$$= \frac{(a\alpha_n)^2}{n^2\pi^2} \left(\frac{b-a}{a}\right)^2$$

are calculated for various $\frac{b}{a}$ from 1.2 to 4 at n=1. The results are listed in Table 1. The ratios are also calculated for various n from 1 to 5 at a fixed value of $\frac{b}{a} = 1.667$. These are listed in Table 2.

For large t the first term is sufficient to accurately estimate y in the summation. For hollow cylinders taking the first term only and taking the logarithm

$$\ell n\ y \simeq \ell n \left[-2\ \ell u \left(\frac{b}{a}\right) \frac{Jo\ (a\alpha_1)\ Jo\ (b\alpha_1)}{Jo\ (a\alpha_1) - Jo^2\,(b\alpha_1)}\right] - \alpha_1{}^2 Dt$$

The observed slope $[\partial \ell n\ y/\partial t]$, is $\left[\frac{\partial \ell u\ y}{\partial t}\right] = \alpha_1{}^2\ D_{cyl}$

Then diffusivity is

$$D_{cyl} = -\frac{1}{\alpha_1{}^2} \left[\frac{\partial \ell n\, y}{\partial t}\right]$$

Similar calculations for planar geometry give

$$\frac{\partial \ell n\ y}{\partial t} = -\frac{\pi^2 Dt}{(b-a)^2}$$

and

$$D_{planar} = -\frac{(b-a)}{\Pi^2}\left[\frac{\partial \ell n\, y}{\partial t}\right]$$

The diffusivity ratio for the two geometries is

$$\frac{D_{planar}}{D_{cyl}} = \frac{(a\alpha_1)^2}{\pi^2}\,\frac{(b-a)^2}{a^2}$$

For b/a = 1.667, $a\alpha_1$ is 4.69706 and the diffusivity ratio is

$$D_{cyl} = D_{planar}/0.9935$$

The true diffusivity of a hollow cylinder should be about 0.65% larger than the value calculated by assuming a planar geometry.

The asymptotic value of y is derived in detail in Appendix B, and is given by

$$y_{asym} = -2\,\frac{\sqrt{k}\;\ell nk}{k-1}\,\Sigma\,(-1)^n \exp\left[-\frac{n^2\pi^2 Dt}{(b-a)^2}\right]$$

Where k = b/a. For planar of which a and b go to infinity and k approaches 1

$$\lim_{k\to 1}\frac{\ln k}{k-1} = 1$$

and

$$\lim_{k+1} y_{cyl} = y_{plann}$$

APPENDIX A

The solution of Diffusion Equation of Hollow Cylinder for "Pump-out" and "Breakthrough" cases.

The diffusion equation for the cylindrical coordinate is

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial c}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 c}{\partial \Theta^2} + \frac{\partial^2 c}{\partial Z^2} \qquad \text{A-1}$$

For the radial flow, the concentration is not a function of Θ and Z. At steady state, we have

$$\frac{\partial Cs}{\partial t} = 0 = \frac{\partial}{\partial r}\left(r\frac{\partial Cs}{\partial r}\right) \qquad \text{A-2}$$

The solution of this equation is

$$Cs = \frac{C_1 \ \ell n\ (b/r) + C_2 \ell n\ (r/a)}{\alpha n\ (b/a)} \qquad \text{A-2}$$

by boundary conditions

$$\text{at } r = a \quad C = C_1$$

and

$$\text{at } r = b \quad C = C_2 \qquad \text{A-4}$$

The flow rate at steady state Js is

$$Js = -2\ \pi r\ D\left(\frac{\partial c}{\partial r}\right) = -\frac{2\pi D\ (C_2 - C_1)}{\ell n\ (b/a)} \qquad \text{A-5}$$

The general solution of equation A-1 for the radial flow[2] is

$$\bar{C} = \frac{\pi^2}{2}\sum_{n=1}^{\infty}\frac{\alpha_n^{\ 2}\ Jo\ (a\alpha_n)}{Jo^2\ (a\alpha_n) - Jo^2(b\alpha_n)}\ e^{-\alpha_n^{\ 2}Dt}\ Uo\ (r\alpha_n)\int_o^b rF(r)\ Uo(r\alpha_n)\ dr$$

$$-\ \pi\sum_{n=1}^{\infty}\frac{\{C_2\ Jo(a\alpha_n) - C_1 Jo\ (b\alpha_n)\}Jo\ (a\alpha_n)}{Jo^2\ (a\alpha_n) - Jo\ \ (b\alpha_n)}\ Uo\ (r\alpha_n)_e - \alpha_n^{\ 2}\ Dt$$

$$+\ \frac{C_1\ \ell n\ (b/r) + C_2\ \ell n\ (r/a)}{\ell n\ (b/a)} \qquad \text{A-6}$$

Where Jo is a Bessel of the first kind,

$$Uo\ (ra_n) = Jo\ (\alpha_n r)\ Yo\ (\alpha_n b) - Jo(\alpha_n b)\ Yo\ (\alpha_n r) \qquad \text{A-7}$$

$$Uo\ (b\alpha_n) = Uo\ (b\alpha_n) = 0 \qquad \text{A-8}$$

Where Yo is Bessel function of the second kind, F (r) is the concentration of t=0, and α_n's are the solution of equation A-8. For the "breakthrough case," the boundary conditions are

$$\begin{array}{ll} t = 0 & F\ (r) = 0 \\ t > 0 & C\ (r=a) = C_1 = 0 \\ & C\ (r=b) = C_2 \end{array} \qquad \text{A-9}$$

By the equation A-6, the concentration is

$$C = \frac{C_2\ \ell n\ (r/a)}{\ell n\ (b/a)} - \pi\ C_2 \sum_{n=1}^{\infty} \frac{Jo^2\ (a\alpha_n)}{Jo^2(a\alpha_n) - Jo^2(b\alpha_n)}\ Uo\ (r\alpha_n) e^{-\alpha_n^2\ Dt} \qquad \text{A-10}$$

The flow rate is

$$J = -\ 2\ \pi D\ r\ \frac{\partial C}{\partial r}$$

$$\cong 2\pi\ D \frac{C_2}{\ell n\ (b/a)} + 4\pi^2\ C_2 D \sum_{n=1}^{\infty} \frac{Jo^2(a\alpha_n)}{Jo^2(a\alpha_n) - Jo^2(b\alpha_n)}\ e^{-\alpha_n^2\ Dt} \quad - \frac{2}{\pi}\ \frac{Jo\ (b\alpha_n)}{Jo\ (a\alpha_n)}$$

$$= Js - 4\ \pi D\ C_2 \sum_{n=1}^{\infty} \frac{Jo\ (a\alpha_n)\ Jo\ (b\alpha_n)}{Jo^2(a\alpha_n) - Jo^2(b\alpha_n)}\ e^{-\alpha_n^2\ Dt} \qquad \text{A-11}$$

or

$$\frac{Js - J\ (t)}{Js} = -2\ \ell n\ (b/a) \sum_{n=1}^{\infty} \frac{Jo\ (a\alpha_n)\ Jo\ (b\alpha_n)}{Jo\ (a\alpha_n) - Jo\ (b\alpha_n)}\ e^{-\alpha_n^2 Dt} \qquad \text{A-12}$$

For the "pump-out" case, the bondary conditions are:

$$\begin{array}{ll} t = 0 & F(r) = Cs\ \dfrac{C_2\ \ell n\ (r/a)}{\ell n\ (b/a)} \\ & C_1 = 0 \\ t > 0 & C\ (r=a) = C_1 = 0 \\ & C\ (r=b) = C_2 = 0 \end{array} \qquad \text{A-13}$$

We have

$$rF(r) = \frac{C_2 \ \ell n \ (r/a)}{\ell n \ (b/a)} \qquad \text{A-14}$$

$$\int_a^b rF(r)\, U_o(r\alpha_n)\,dr = \frac{C_2}{\ell n(b/a)}\int_a^b r\ell nr\, U_o\, dr - \frac{C_2 \ell n\ a}{\ell n(b/a)}\int_a^b rU_o\, dr$$

$$= \frac{C_2}{\ell n\ (b/a)} \ \frac{2\ \{Jo(a\alpha_n)\ \ell nb - Jo(b\alpha_n)\ \ \ell n\ \ a\}}{\pi\ \alpha^2\ Jo\ (a\alpha_n)} - \frac{C_2 \ell n\ a}{\ell n(b/a)}\ \frac{2\ \{Jo\ (a\alpha_n - Jo\ (b\alpha_n)\}}{\pi\alpha^2\ Jo(a\alpha_n)}$$

$$= \frac{2\ C_2}{\pi\alpha_n^{\ 2}} \qquad \text{A-15}$$

and

$$C = \pi C_2 \sum_{n=1}^{\infty} \frac{Jo^2\ (a\alpha_n)}{Jo^2(a\alpha_n) - Jo^2(b\alpha_n)}\ e^{-\alpha_n^{\ 2}\ Dt}\ Uo\ (r\alpha_n) \qquad \text{A-16}$$

The flow rate is

$$J = 2\pi r\ \frac{\alpha c}{\alpha r}$$

$$= 2\pi D\ \ \pi C_2 \sum_{n=1}^{\infty} \frac{Jo^2\ (a\alpha_n)}{Jo^2\ (a\alpha_n) - Jo^2\ (b\alpha_n)}\ \ e^{-\alpha_n^{\ 2}\ Dt}\ r\left(\frac{\partial U_0}{\partial r}\right) \qquad \text{A-17}$$

But

$r\left(\frac{\partial U_0}{\partial r}\right)$ is

$$r\left(\frac{\partial U_0}{\partial r}\right)_a = -\frac{2}{\pi}\ \frac{Jo\ (b\alpha_n)}{Jo\ (a\alpha_n)} \qquad \text{A-18}$$

Then we have

$$J = 4\ \pi DC_2 \sum_{n=1}^{\infty} \frac{Jo\ (a\alpha_n)\ Jo\ (b\alpha_n)}{Jo^2(a\alpha_n) - Jo^2(b\alpha_n)}\ e^{-\alpha_n^{\ 2}\ Dt} \qquad \text{A-19}$$

or

$$\frac{J\ (t)}{Js} = -\ 2\ \ell n\ (b/a) \sum_{n=1}^{\infty} \frac{Jo\ (a\alpha_n)\ Jo\ (b\alpha_n)}{Jo^2(a\alpha_n) - Jo^2(b\alpha_n)}\ e^{-\alpha_n^{\ 2}\ Dt} \qquad \text{A-20}$$

This is the same as equation A-12, by combining equations A-12 and A-20 we have

$$y = -2 \ \ell n \ (b/a) \sum_{n=1}^{\infty} \frac{Jo \ (a\alpha_n) \ Jo \ (b\alpha_n)}{Jo^2(a\alpha_n) - Jo^2 \ (b\alpha_n)} \ e^{-\alpha_n^{\ 2} Dt} \qquad \text{A-21}$$

where $y = J\ (t)/Js$ for "pump-out" case

and $y = [Js - J\ (t)]/Js$ for the "breakthrough" case.

The plannar solution is known to be

$$y = -2 \sum_{n=1}^{\infty} (-1)^n \exp \left[- \frac{n^2 \pi^2}{d^2} Dt \right] \qquad \text{A-22}$$

where $d = b-a$.

APPENDIX B ASYMPTOTIC SOLUTION

For large x Jo (x) and Jo (x) are

$$Jo\ (x) \sim \frac{2}{\sqrt{\pi x}} \cos\left(x - \frac{\pi}{4}\right) \qquad \text{B-1}$$

$$yo\ (x) \sim \frac{2}{\sqrt{\pi x}} \sin\left(x \frac{\pi}{4}\right) \qquad \text{B-2}$$

The equation A-7 by this asymptotic

$$Jo\ (x)\ yo\ (kx) - Jo\ (kx)\ yo\ (x) = 0$$

$$= \frac{2}{\pi x}\left[\frac{1}{\sqrt{x}} \quad \cos\ (x - \frac{\pi}{4})\ \sin\ (kx - \frac{\pi}{4}) - \cos\ (kx - \frac{\pi}{4}) \sin\ (x - \frac{\pi}{4})\right.$$

$$= \frac{2}{\pi x}\ \frac{1}{\sqrt{x}} \sin\ \left((k-1)\ x\right) \qquad \text{B-3}$$

The solution is

$$x_n = \frac{n\pi}{k-1} \qquad \text{B-4}$$

where $k = \frac{b}{a}$. And α_n is by A-8

$$\alpha n = \frac{x_n}{a} \qquad \text{B-5}$$

Also we have

$$Jo\ (x_n)\ Jo\ (kx_n) = \frac{2}{x_n \pi}\ \frac{1}{\sqrt{k}} \cos\left(x_n - \frac{\pi}{4}\right)\ \cos\ \left(kx_n - \frac{\pi}{4}\right)$$

$$= (-1)^n \frac{2}{\pi x_n}\ \frac{1}{k} \cos^2\ \left(x_n - \frac{\pi}{4}\right) \qquad \text{B-6}$$

$$Jo^2\ (x_n) = \frac{2}{\pi x_n}\ \cos^2\left(x_n - \frac{\pi}{4}\right) \qquad \text{B-7}$$

and

$$Jo^2\ (kx_n) = \frac{2}{\pi x_n\ k}\ \cos^2\ \left(x_n \frac{\pi}{4}\right) \qquad \text{B-8}$$

By equations B-6, B-7, B-8 and A-21 we have

$$y_{assym} = -2\ \ell nk\ \Sigma(-1)^n\ \frac{\frac{1}{\sqrt{k}}}{1 - \frac{1}{k}} \exp\ \left[-\frac{n^2\ \pi^2 Dt}{d^2}\right] \qquad \text{B-9}$$

By comparison with A-22 we have

$$y_{asymp} = \left(\frac{\sqrt{k}\ \ell nk}{k-1} \quad y_{plann} \right) \qquad \text{B-10}$$

For the limiting case where $k \to 1$, a and b go to infinity, the cylindrical geometry approaches planar. By considering both the relationship

$$\lim_{x \to o} \frac{\ell n\ (1+x)}{x} = 1 \qquad \text{B-11}$$

and equation B-10

$$\frac{\ell im}{k \to 1} y_{cylin} = \frac{\ell im}{k \to 1} y_{asymp}$$

$$= y_{plan} \qquad \text{B-12}$$

REFERENCES

1. J. Crank, "The Mathematics of Diffusion", Oxford at the Clarendon Press, 1956

2. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids", Oxford, 1947

3. R. M. Barrer, "Diffusion in and through Solids", Cambridge, 1951

4. M. Abramowitz and I. A. Stegun, Editor, " Handbook of Mathematical Functions", Dover Publications, Inc. New York 1965

TABLE 1

EXPONENT OF THE FIRST TERM

$\frac{b}{a}$	$a\alpha_1$	$\frac{\alpha_1^2(b-a)^2}{\pi^2}$	$\left[1-\frac{\alpha_1^2\ (b-a)^2}{\pi^2}\right]$
1.2	15.7014	0.99916	0.00084
1.5	6.2702	0.99587	0.00413
1.6667	4.69706	0.99350	0.00650
2.0	3.1230	0.98820	0.01180
3.0	1.5485	0.97181	0.02819
4.0	1.0244	0.95693	0.04307